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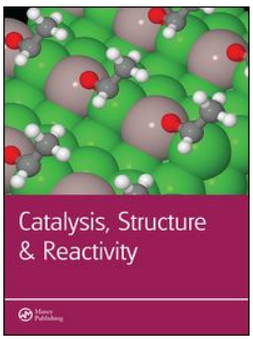

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Original Research Paper

Re-dispersion of gold supported on a 'mixed' oxide support

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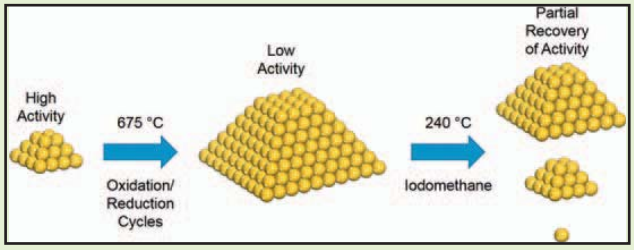
Abstract The ability to reactivate, stabilize and increase the lifetime of gold catalysts by dispersing large, inactive gold nanoparticles to smaller nanoparticles provides an opportunity to make gold catalysts more practical for industrial applications. Previously it has been demonstrated that mild treatment with iodomethane (*J. Am. Chem. Soc.*, 2009, 131, 6973; *Angew. Chem. Int. Ed.*, 2011, 50, 8912) was able to re-disperse gold on carbon and metal oxide supports. In the current work, we show that this technique can be applied to re-disperse gold on a 'mixed' metal oxide, namely a mechanical mixture of ceria, zirconia and titania. Characterization was conducted to guage the impact of the iodomethane (CH_3I) treatment on a previously sintered catalyst.



Keywords Gold catalysts, Catalyst regeneration, Gold re-dispersion, CO oxidation

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Introduction

Since the 1980s when it was first demonstrated that gold was catalytically active,[1,2] there has been an ever increasing number of reports on gold catalyzed reactions.[3–5] The utilization of gold catalysts has been spurred on by advances in the ability to produce small nanoparticles, which have been found to be catalytically active in a range of reactions in sectors as varied as environmental remediation and bulk/pharmaceutical chemical production.[3,6]

It has been reported that the size of the deposited gold nanoparticles as well as the nature of the metal-support interaction are strongly linked to the catalytic performance.[3,7–9] However, while these systems often show excellent initial activity and selectivity, it is known that gold catalysts typically have low stability under thermal treatment and/or reaction conditions.[6] This deactivation has been proposed to be associated with surface poisoning, loss of interaction between gold and the support, as well as sintering of the gold nanoparticles.[6] Hence, if gold catalysts are to have a long-term future in industrial applications, methods of stabilization and/or reactivation need to be developed in order to make this feasible.[3]

It has been reported previously that Au/C catalysts could be activated during the carbonylation of methanol to methyl acetate in the presence of iodomethane (CH_3I).[10,11] This activation has been attributed to increased gold nanoparticle dispersion from clusters of >10 nm to gold dimers/trimers, which are stabilized by iodine. Owing to the harsh conditions (240°C and 16 bar), this process may not be applicable for all gold catalytic systems; however, it has recently been demonstrated that atmospheric pressure treatments using iodomethane for gold dispersion provide a treatment to atomically disperse these large particles of gold on both carbon[6,12] and metal oxide supports.[3]

While gold catalysts supported on both carbon and metal oxides are common, there are a range of mixed metal oxides which have been found to provide additional desirable properties over pure metal oxides. For example, mixed ceria–zirconia supports possess the ability to switch between Ce^{3+} and Ce^{4+} due to elevated oxygen storage and oxygen transport capacity.[13] It has been reported that catalysts supported on mixed metal oxides can be more active

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than those supported on individual pure metal oxides.[13,14] Some of the reactions for which gold catalysts supported on mixed metal oxides have been found to be particularly active include CO oxidation,[14,15] water gas shift (WGS)[16,17] and preferential oxidation of CO (PROX).[18,19]

The catalytic oxidation of carbon monoxide is an important reaction in applications including cold start exhaust emission control for automobiles, respirators and clean hydrogen production. Mixed oxide catalysts have been reported for CO oxidation,[20,21] the activity of which have been found to improve upon doping with gold.[14,15] Au/$CeZrTiO_x$ is a mixed oxide catalyst which has been designed for applications in hydrocarbon oxidation as well as methanol, methane and carbon monoxide fuel cells.[22]

To date, there has been no reported application of the iodomethane treatment to gold catalysts supported on mixed metal oxide supports in order to tailor the properties of the catalyst. Herein, we report the effect of iodomethane treatment on the activity of a previously sintered 1.0 wt% Au/$CeZrTiO_x$ catalyst for CO oxidation.

Experimental

Catalyst preparation

To deposit gold on the catalysts, a LabMax®(Mettler-Toledo, USA) automated laboratory reactor system with a 500 cm^3 glass reactor was used. This system provides constant reactor temperature, constant pH of the reaction media, uniform constant intensive mixing and simultaneous controlled dosing of liquid components. The support was a mechanical mixture with composition CeO_2:ZrO_2:TiO_2 = 5.5 : 2.5 : 2.0.

Before gold deposition, the support was subjected to ultrasonic treatment for 30 min and dried at 120°C for 4 h. This was to ensure sufficient mixing of the support in order to facilitate a homogeneous gold dispersion. Gold was deposited from an aqueous solution of $HAuCl_4$ (Acros Organics, Belgium) at 80°C, with intensive mixing. An aqueous solution of magnesium citrate was added to maintain the pH of the liquid phase at 8.0 ± 0.1. At the end of the precipitation process, the suspension was aged for 1 h at 60°C. The suspension was then filtered and the catalyst (~ 10 g) was washed with 1 L of warm distilled water (50°C) to remove Cl^- ions. The powder was then dried for 4 h at 120°C and then calcined by ramping the temperature at 10°C min^{-1} to 550°C before being held at this temperature for 6 h in air. As gold clusters are known to sinter with prolonged heating at temperatures greater than 395°C,[23] the sintered catalyst was prepared by cycling between reducing and oxidizing environments at 675°C.

Treatment with iodomethane

Iodomethane (Aldrich, USA) treatments were performed in a quartz reactor (O.D. 6 mm) using *ca.* 100 mg of catalyst. The quartz reactor was heated in flowing argon (40 cm^3 min^{-1}) with a tubular furnace and the temperature was increased to the set temperature (240°C) using a ramp rate of 10°C min^{-1}. Once at temperature, the iodomethane/argon was admitted to the reactor with a steady flow of 40 cm^3 min^{-1} iodomethane/argon with the vapor pressure of the iodomethane determined by a saturator held at 25°C, equating to 0.14 cm^3 min^{-1} of iodomethane.

Characterization

Inductively coupled plasma – optical emission spectrometry (ICP-OES) was used to quantify the concentration of gold on the fresh, sintered and iodomethane-treated catalysts. Sodium peroxide was used to remove the gold from the support, and a 4300 DV ICP-OES (Perkin Elmer, USA) was used to quantify the amount of gold for all the catalysts. The Brunauer, Emmett and Teller (BET) surface area characterisation was obtained using a Tristar 3000 (Micromeritics, USA) gas adsorption analyzer using N_2 to determine average pore volume. The sample was subjected to vacuum to remove any impurities, such as water, followed by flushing with helium gas for 2 min before the vacuum was then reintroduced.

Raman analysis of the samples was carried out in order to determine any effect of the treatments on the support. A Ramanstation fibre optic system (Avalon, UK) was used employing a 785 nm laser. Spectra were accumulated for 90 s and the reported data was averaged over five scans.

High Resolution Transmission Electron Micrographs were collected on a 200 kV JEM-2010F (JOEL, USA) instrument with a structural resolution of 0.19 nm at Scherzer defocus conditions. Scanning Transmission Electron Microscopy (STEM) images were recorded in the same instrument using a high-angle annular dark-field (HAADF) detector and an electron beam probe of 0.5 nm.

Powder X-Ray diffraction (XRD) measurements were carried out using an X'Pert Pro X-ray diffractometer (PANalytical, USA). The X-ray source used was copper K_α with a wavelength of 1.5405Å. Diffractograms were collected from 20° to 85° with a step size of 0.04°.

Diffuse reflectance ultraviolet–visible (DRUV) spectroscopy measurements were performed using a Lambda 650S UV–vis spectrophotometer (Perkin Elmer, USA) equipped with a Harrick stage chamber and an integrating sphere detector Magnesium oxide was used as the `auto zero' reference for all sample spectra.

CO oxidation

In order to probe the ability of iodomethane to improve the activity of the sintered catalyst, CO oxidation was performed as this is known to require small gold nanoparticles for good activity.[24–26] Activity tests were performed in a quartz tubular reactor (O.D. 10 mm). One hundred milligrams of catalyst was held in place between two plugs of quartz wool and a thermocouple was placed in the center of the catalyst bed. The temperature of the reactor was controlled using a tubular furnace with a proportional-integral-derivative (PID) controller and the reaction was investigated by ramping the temperature to 500°C. The reactants and products were analyzed at the outlet of the reactor by gas chromatography (Clarus 500, Perkin Elmer) with a FID and TCD. The gas feed consisted of 2% CO, 2% O_2, 0.5% Kr and 95.5% Ar with a total flowrate of 100 cm^3 min^{-1}.

Results and discussion

Fig. 1 shows the comparison of the CO oxidation activity for the fresh 1.0 wt% Au/$CeZrTiO_x$ catalyst, sintered catalyst, iodomethane-treated sintered catalyst and support. The support showed 50% conversion at 400°C. As expected, on addition of gold, significantly higher activity was observed

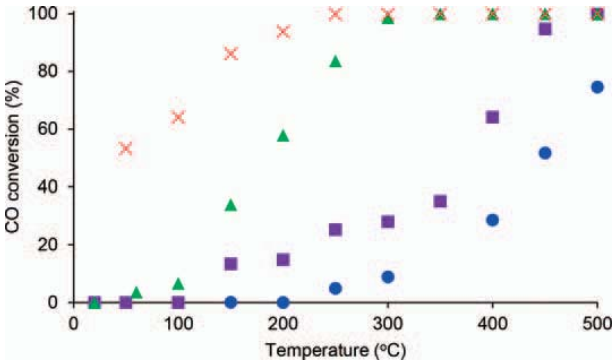

Figure 1 CO conversions as a function of temperature for the Au/CeZrTiO$_x$ catalyst samples; support (●), fresh (x), sintered (■) and sintered/CH$_3$I (▲)

with the fresh catalyst showing 50% conversion at 50°C. On sintering, the activity of the catalyst significantly decreased only achieving 50% conversion at ~375°C, i.e. close to that found for the support only. Importantly, after the sintered catalyst was treated with iodomethane, there was a marked increase in the activity with 50% conversion observed at ~175°C. In order to probe the reason for the enhancement following iodomethane treatment, the catalyst structure and textural characteristics were examined.

The nature of the catalyst (mechanical mixture of three metal oxide supports) has made material characterization difficult, and as such it has been a case of using a process of elimination in order to gain an understanding of the effect of the iodomethane treatment. Additionally, for purposes of clarity, while results from each of the techniques are discussed below, only results from techniques where discernible changes were observed are reported in the table and figures.

Gold elemental analysis for the catalysts are summarized in Table 1. These results show that the iodomethane treatment did not significantly change the gold loading. This is consistent with the previously reported data on carbon supported and metal oxide supported catalysts, where little leaching/removal of gold was observed following treatment with iodomethane even at 240°C.[3] Therefore, any changes observed with other characterization methods can be associated with structural changes in the gold particles rather than due to a significant loss of gold content.

Table 1 summarizes the BET surface areas of the studied systems. Comparing the BET surface area of the fresh catalyst to the support alone shows a small increase in surface area. However, on sintering the sample the surface area decreases from 116 to ~8 m^2 g^{-1} coupled with a significant decrease in the pore volume of the catalyst. This is reversed to some degree

Table 1 Gold elemental analysis and textural characteristics of the Au/CeZrTiO$_x$ catalyst samples

Catalyst Sample	Au content (wt-%)	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
Support	–	111.0	0.20	6.7
Fresh	0.98	116.0	0.18	6.6
Sintered	1.02	7.6	0.02	16.1
Sintered/CH$_3$I	1.00	24.6	0.08	14.2

on treatment with iodomethane where the surface area is found to increase to ~25 m^2 g^{-1}; however, this is still lower than that of the original fresh catalyst.

The XRD patterns for each catalyst system (Fig. 2) shows reflections which can be attributed to the individual components of the support; i.e. titania (at 25.2, 47.4 and 69.4°), ceria (at 28.5, 59.0, 76.6 and 79.0°) and zirconia (33.1 and 56.3°). On deposition of gold onto the support a change in the mixed oxide particle size is observed. This is shown by examining the dominant reflection for ceria at 28.5°, titania at 47.4° and zirconia at 56.3°. In each case, a small shift in the maximum, of ~0.3°, was observed associated with a decrease in the lattice spacing. The more striking effect is the broadening of the oxide features. For example, the full width at half maximum (FWHM) increased from ~0.3° to 1.1°, 1.6° and 1.8° for the ceria, titania and zirconia features, respectively. This would indicate a decrease in particle size of the oxide crystallites. This may be responsible for the small increase in BET surface area from the support to the fresh catalyst sample. It is also worth noting that, after the gold sintering procedure, the FWHM of these three reflections decreases to 0.7°, 1.1° and 0.8°. This is indicative of a growth in the oxide particle size which shows that the catalyst support also underwent sintering. The increase in the particle size may be contributing to the sharp decrease in the BET surface area; however, it is unlikely to be the predominant cause due to the large change observed. The latter is more likely to be due to the loss of pores as a result of the collapse of the pore structure.

It should be noted that the XRD patterns for all the gold based samples had weak diffraction features at 38.4° and 44.5° which can be attributed to gold. However, due to the low signal to noise ratio and interference from a weak support feature, in the case of the peak at ~38°, this did not allow accurate measurement of the gold particle size. It is interesting to note that, unlike in the previously reported systems where the iodomethane treatment resulted in an almost complete absence of gold diffraction features,[3,6,12,27] the gold features remained. This may be associated with some of the gold not dispersing following the treatment as the diffractograms are always dominated by the largest particle size.

In order to further probe the changes in the support and the gold following the treatment, Raman and TEM studies

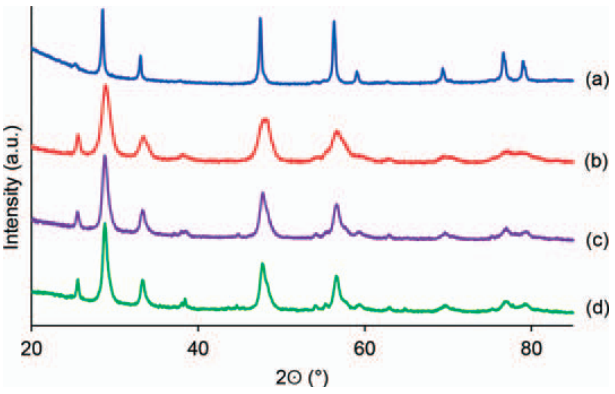

Figure 2 X-ray diffractograms for the Au/CeZrTiO$_x$ catalyst samples; support (*a*), fresh (*b*), sintered (*c*) and sintered/CH$_3$I (*d*)

were undertaken. There were no discernible changes in the band frequencies or the FWHM observed in the Raman spectra, showing little influence of the iodomethane treatment on the phase of the support, in agreement with the XRD patterns. Similarly, the TEM did not show any significant changes to the structure of the support and only dramatic changes of the particle size could be deciphered. The TEM did show large gold particles, the smallest average size of which were of the order of 25–50 nm; however, due to the complex chemical composition of the support (three cations) and the poor *Z* contrast between the gold and the ceria element of the support, the presence of small gold particles or clusters (<0.5 nm) cannot be dismissed. From energy-dispersive X-ray (EDX) spectroscopy, the gold is evenly distributed across the support and it does not appear that the gold has preferentially been located on one elemental phase over the others. However, the TEM was able to determine that no particles in the size range of 1–5 nm are likely to be present. Therefore, it was not possible to determine accurate particle size distribution.

In order to probe the smaller gold particles, diffuse reflectance UV–vis spectroscopy (DRUV) was employed as this is sensitive to the small rather than the large particles, in contrast with the XRD technique. Diffuse reflectance ultraviolet–visible height normalized spectra for each of the gold based materials are shown in Fig. 3. A broad characteristic gold adsorption band for the fresh and sintered catalyst, with the maximum at ~600 nm was observed; however, on treatment of the sintered catalyst with iodomethane, this feature disappears and there is an increase in the UV–vis absorption at lower wavelengths. The peak ~600 nm has been attributed to the plasmon resonance of gold metal nanoparticles[3,28,29] whereas absorption at lower wavelengths is owing to ionic gold ($\lambda \leq 250$ nm) and small clusters of gold ($280 \leq \lambda \leq 380$ nm).[30,31] The disappearance of the peak at 600 nm and the increase in absorption at around below 500 nm indicate dispersion of some of the gold nanoparticles into small clusters following treatment of the sintered sample with iodomethane.[3] Interestingly, these nanoparticles are present in both the fresh and sintered catalysts; however, as shown by the high activity of the fresh catalyst for CO oxidation, it is likely that this catalyst also has well dispersed gold. It is not possible to probe the presence of the very smallest particles/ionic gold

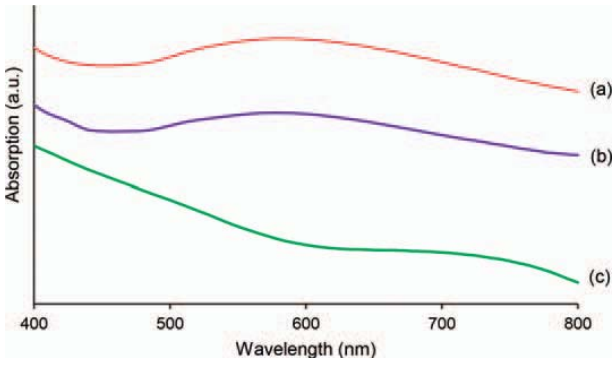

Figure 3 Diffuse reflectance ultraviolet–visible (DRUV) spectra for the Au/CeZrTiO$_x$ catalyst samples; fresh (*a*), sintered (*b*) and sintered/CH$_3$I (*c*)

owing to the presence of the titania and its strong absorption band below 330 nm.[3]

The high CO oxidation activity of the fresh catalyst is likely to be owing to the presence of highly dispersed gold, as reported previously,[24–26] and high surface area of the support compared with the sintered catalyst. From the DRUV, it is clear that the iodomethane treatment of the sintered catalyst resulted in a reduction of gold particle size and this is reflected in the increased activity of the iodomethane-treated sintered sample for CO oxidation compared to the sintered catalyst, as well as an increase in the surface area of the sample. An increase in support surface area alone does not promote the catalysis since the support has a much larger surface area than the sintered and iodomethane-treated sintered samples, yet the support has a far inferior activity for the CO oxidation reaction than any of the catalyst samples. From previous studies it is known that the iodomethane treatment can result in almost complete dispersion of gold into atoms, dimers and trimers and this is likely to be the case in these samples too. However, while significantly higher activity is observed for the treated sintered catalyst compared with the system before treatment, the activity of the original catalyst is not recovered. This may be due to residual halide being present on the surface of the catalyst which is known to poison gold based CO oxidation catalysts.[32–34] In addition, the surface area and pore volume of the sintered catalyst following treatment is much lower than that of the fresh catalyst resulting in far fewer accessible active sites.

Conclusion

The reported results showed the applicability of iodomethane treatments for the reactivation of gold, probably owing to re-dispersion of gold particles in a mechanically mixed oxide support, namely ceria–zirconia–titania. The TEM analysis suggests that there is little difference in the samples as a consequence of the treatment with iodomethane. The DRUV does indicate that iodomethane-treated sintered sample did result in gold redispersion. Importantly, iodomethane treatment of the sintered sample was found to reactivate the deactivated sintered catalyst for CO oxidation and significantly reduced the temperature for 50% conversion by 200°C. Although the catalyst was not as active as the fresh catalyst treatment either owing to the presence of surface halide or the smaller surface area, this is the first time that an effectively completely deactivated gold catalyst has been reactivated using a technique which does not reduce the amount of gold on the surface of the catalyst. This treatment provides a significant opportunity to reactivate gold based catalysts without the need to remove the catalyst from the reactor system.

Notes

Supporting data are openly available on Queen's University Research Portal http://pure.qub.ac.uk./portal/en/datasets.

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